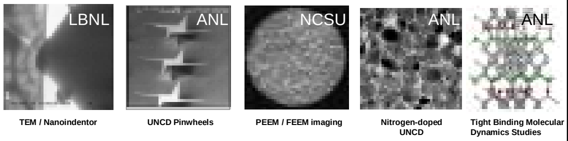
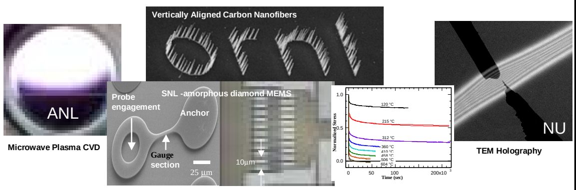


Synthesis and Processing of Carbon-based Nanostructured Materials



Outline

- Vision/Impact
- Project Participants
- Proposed Project Activities:
  - Task 1: Fundamental Mechanical and Tribological Properties
    - A. Mechanical and tribological properties of carbon-based thin films
    - B. Materials issues in carbon-based MEMS devices
  - Task 2: Fundamental Transport Properties
    - A. Electronic properties of carbon based materials
    - B. Carbon-based Nanocomposites
- Technological Applications and Industrial Partners
- Management Plan & Budget
- Summary

Vision/Impact

Vision

- **Advance the science of carbon-based materials**
  - Fundamental phenomena induced by unique microstructures
  - New generation of micro- and nano-multifunctional devices
- **Effectively couple existing programs on carbon-based materials**

Impact

- **New Science**
  - Nanoinstrumentation
  - Mechanical/Tribological/Electronic studies of Nanostructured Materials
- **Novel nanotechnologies**
  - Carbon-based MEMS processing techniques
  - Carbon Nanocomposites

Center Participants

ARGONNE NATIONAL LABORATORY — D.M. Gruen, J.A. Carlisle, D.C. Mancini, A. Erdemir, O. Auciello, S.R. Phillpot, L.A. Curtiss

Sandia National Laboratories — T. A. Friedmann, M.T. Dugger, T.E. Buchheit, M.P. de Boer

D.H. Lowndes, V.I. Merkulov

E.A. Stach

NC STATE UNIVERSITY — R. J. Nemanich

NORTHWESTERN UNIVERSITY — V.P. Dravid, R.S. Ruoff

Industrial Collaborators — UHV Technologies, Indel, Flow-Serve, Second-Sight, Raytheon, LiteMatrix, Northrop Grumman, IPLAS

Interdisciplinary Collaboration to Increase Understanding of Carbon-based Materials Science

Two tasks focused on areas where basic understanding can be accelerated by teaming.

Task 1: Fundamental Mechanical and Tribological Properties

A. Materials issues in carbon-based MEMS devices
B. Mechanical and tribological properties of carbon-based thin films

Task 2: Fundamental Transport Properties

A. Electronic properties of carbon based materials
B. Carbon-based Nanocomposites

Common theme
Understanding carbon-based materials at the micro- and nano-scale.

Task 1A Materials Issues in Diamond-based MEMS

Goal

- Develop advanced understanding of carbon-based materials growth
- Integrate carbon materials into devices for basic materials studies

Team

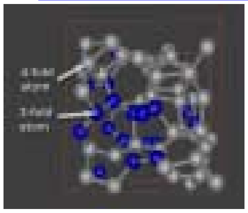
SNL **synthesis and characterization of amorphous diamond films design and fabrication of a-D and UNCD MEMS structure**
ANL **synthesis and characterization of UNCD and ultra-low friction films**
ORNL **growth of aligned carbon nanotubes and carbon nanocomposites**

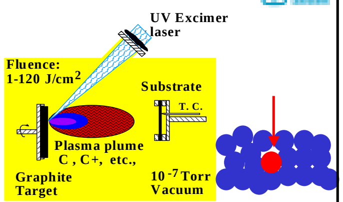
Key Issues

- Real world device fabrication
- Integration strategies for hybrid materials combinations (e.g. UNCD with nanotubes or amorphous diamond)
- Test vehicle design for nanoscale measurements

What is amorphous-Diamond (a-D)?

T.A. Friedmann, (SNL)





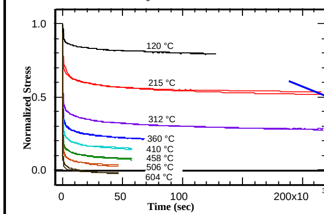
- A nanophase mixture of 3- and 4-fold carbon
- About 70% diamond-like bonds (4-fold) with the balance being 3-fold.
- High modulus (>800 GPa) and hardness (90 GPa)
- Surface roughness ~1Å RMS

- Pulsed-laser deposition
- High fluence (>100 J/cm²) - high ion energy
- The entire film is grown by carbon implantation

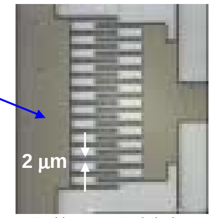
Amorphous diamond for MEMS

$$\sigma(t,T)=\sigma_0+\frac{\varepsilon_{sp^2-sp^3}E}{1-\upsilon}\int_0^\infty N(E_A)\{1-\exp[-\upsilon_0 t\exp(-E_A/k_bT)]\}dE_A$$

T. A. Friedmann, (SNL)



Predictive model for stress relaxation dynamics leads to strain control

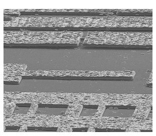


Enables a-D MEMS devices

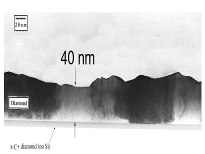
- Growth stresses controlled by annealing
- Use a-D devices as a probe of the nanoscale tribological behavior

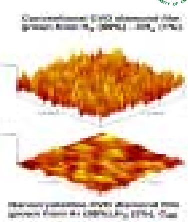
UNCD for MEMS

O. Auciello, J.A. Carlisle and D. M. Gruen (ANL)



UNCD cantilever beams



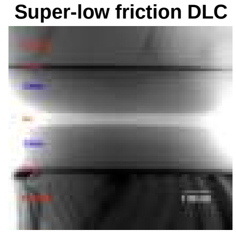


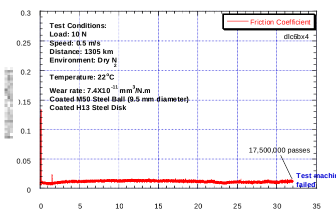
- Smooth surface compared to other CVD synthesis methods.
- Low stress, conformal deposition process
- Mechanical properties depend on grain boundary structure and bonding.

Super-low friction DLC: Origins of ultra-low friction is not understood.

A. Erdemir (ANL)

Super-low friction DLC





- **Structurally amorphous**
- **Superlow friction coefficients (0.001-0.005) in inert gas or vacuum**
- **Extremely low wear: 10^{-9} - 10^{-11} mm³/N.m**
- **Excellent candidate for coating MEMS**

Task 1B Mechanical and Tribological Properties of Carbon-based thin films

Goal

- Understand the role of tribology (e.g. friction, adhesion, and wear) and fracture mechanics at the nanoscale in carbon-based structures.

Team

SNL **Measurement of friction and wear at high shear rate**
Fracture toughness and stiction in carbon-based MEMS

ANL **Computational chemistry for basic understanding of friction and wear**
Understanding super-low friction coatings

LBNL ***in situ* TEM imaging of defect/crack creation during nanoindentation**

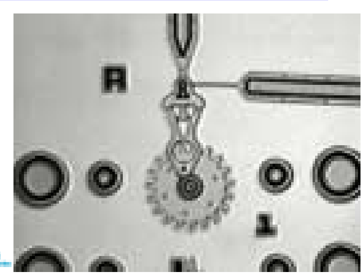
Key Issues

- Friction, wear and adhesion mechanisms in carbon MEMS
- Fundamental limits of strength through control of defects
- Mechanism of low friction in hydrogenated carbon films

Understanding and controlling tribology is critical to the success of MEMS

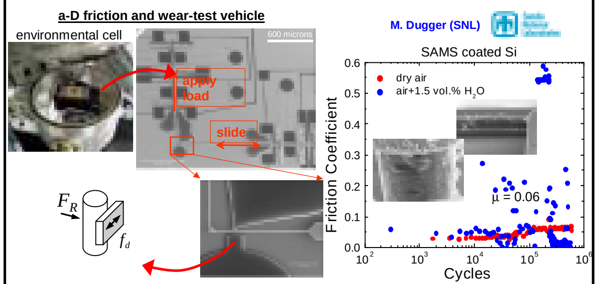
QuickTime Movie

D. Tanner (SNL)



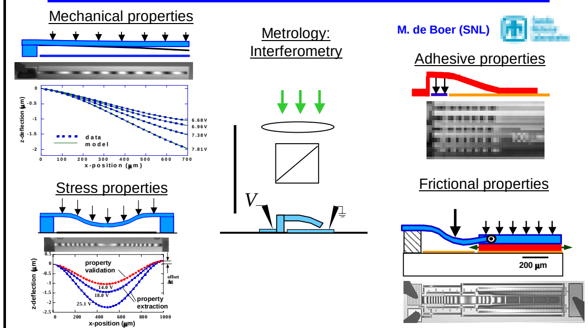
- Friction, wear, and adhesion can limit the performance of Si MEMS
- Diamond-based MEMS offer unique properties that may solve these problems

A unique capability to quantify friction in SMM contacts has been developed.



- Friction and wear must be quantified at force, length and time scales relevant to microsystems
- Leverage test capabilities developed for Si MEMS.

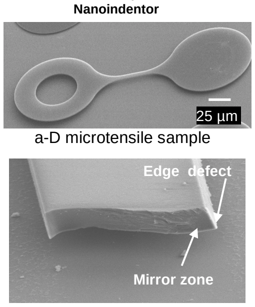
Integrated measurement/modeling capability is used to examine mechanical properties



- Use interferometry and MEMS designs to probe materials properties

Fracture Mechanics at the micro scale.

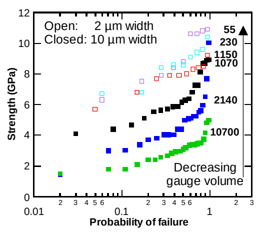
Use lateral force capabilities of a Nanoindentor



a-D microtensile sample

a-D Fracture surface

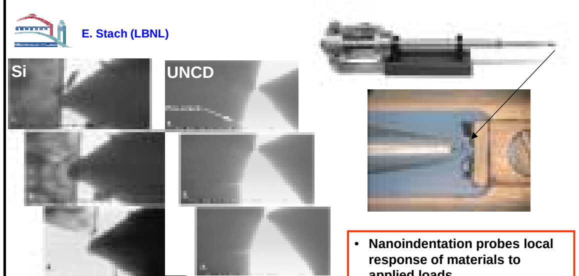
T.E. Buchheit T. A. Friedmann (SNL)



- Determine fracture mechanisms
- Explore limits of strength
- a-D and UNCD films
- Nanotubes (?)

In-Situ TEM indentor for probing nanoscale deformation and fracture mechanisms

E. Stach (LBNL)



cleavage fracture along {111}

No fracture, even with pre-crack

- Nanoindentation probes local response of materials to applied loads.
- *Real time* observations
- Quantitative characterization of load vs. displacement

Outline

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Task 2A Nitrogen-Doped UNCD Films

Goal

- Understand the effect of nitrogen incorporation on the conductivity and field emission properties of UNCD thin films

Team

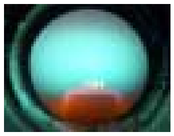
ANL	Synthesis and characterization of nitrogen-doped UNCD films Field emission studies; Molecular dynamics calculations
NCSU	PEEM/FEEM studies of field emission properties
NU	TEM Holography studies to image charge at GBs, E-field of emitters

Key issues

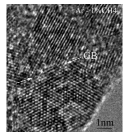
- Grain boundary conduction/morphology in nitrogen-doped UNCD films
- Field Emission properties of nitrogen-doped UNCD films

What is UNCD?

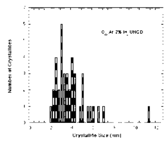
- Ar/CH_4 MPCVD: C_2 dimer growth
- 2-5 nm grain sizes; atomically-abrupt grain boundaries
- Phase-pure (<3% sp^2-bonded carbon)
- Conformal coating, low stress
- Materials Properties:
  - **Mechanical** (high hardness and fracture strength)
  - **Tribological** (low friction, thermal conductance)
  - **Transport** (electronic, thermal)
  - **Electrochemical** (wide working potential window)
  - **Electron Emission** (low, stable threshold voltage)



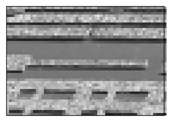
Ar/CH_4 plasma coating W microtips



HRTEM



2-5 nm Grain Sizes



UNCD-MEMS

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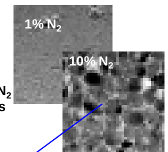
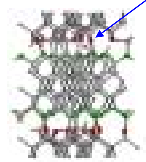
Nitrogen-Doped UNCD: Grain Boundary Conduction?

O. Auciello, J.A. Carlisle and D. M. Gruen (ANL)

MPCVD Ar+CH_4+N_2
C_2, CN Precursors

Morphology Changes

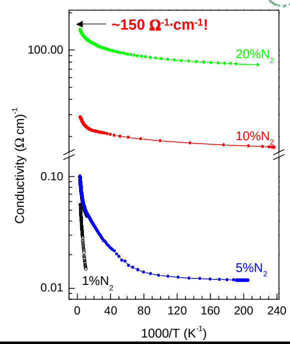




Nitrogen at GBs favored by 4-5 eV

•GB Conduction?
•Morphology?

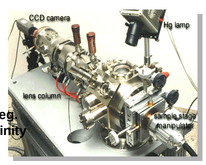
L.A. Curtiss (ANL)



Nitrogen-Doped UNCD: TEAMING

R.J. Nemanich NC STATE UNIVERSITY

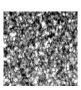
PEEM
FEEM



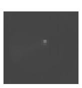
Diamond: Neg. Electron Affinity

Image emission sites in nitrogen-doped UNCD:

Localized at GBs?

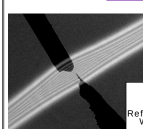


AFM



FEEM

V.P. Dravid NORTHWESTERN UNIVERSITY



TEM Holography

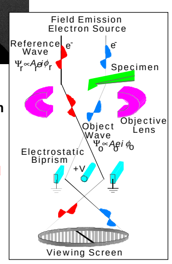


Image variation in electric potential in sample

Charge Localized at GBs?

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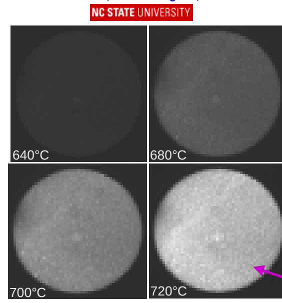
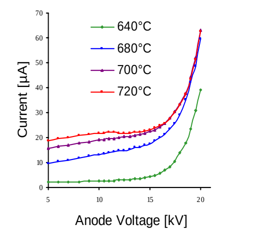
Temperature-dependent FEEM of N-Doped Diamond

Recent Results!!

Franz A.M. Köck, Jacob Garguilo, R.J. Nemanich
NC STATE UNIVERSITY





Images taken at 20µm field of view and channel plate voltage of 1.55kV

Electron emission starts below 640°C and increases with increasing temperature

FIRST observation of uniform emission over the whole surface area

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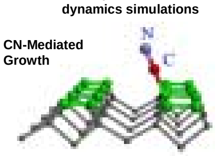
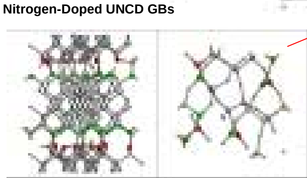
Nitrogen-Doped UNCD: TEAMING Continued

Density functional molecular dynamics simulations

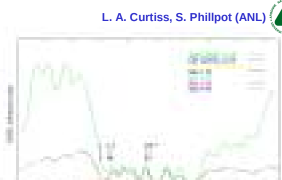
L. A. Curtiss, S. Phillpot (ANL)

CN-Mediated Growth





Nitrogen-Doped UNCD GBs



Local GB Density of States

CSP Project Work:
•Model bigger GBs
•Model transport
Delocalization of GB states

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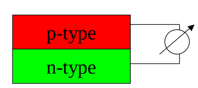
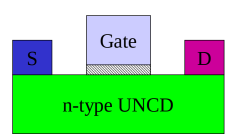
Vision: Enable electronic applications of diamond

- N-type via nitrogen-doping
- P-type via boron-doping
  - Add B_2H_6 to plasma
- Create all-diamond PN grown entirely by MPCVD
  - Study rectification properties
  - UV diode?
- Applications:
  - Photovoltaics
  - Sensors
  - Photonic switches
  - Cold Cathodes
  - Electrochemical electrodes



All-diamond PN junction

Satoshi Koizumi et al., *Science* 292, 1899 (2001)



High-speed / high temperature electronics

K. Tsugawa *et al.*, *Diam. Relat. Mater.* 8, 927 (1999).

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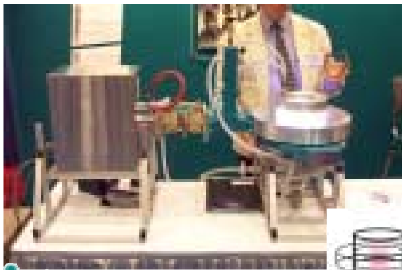
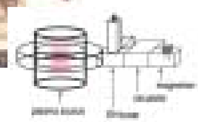
New MPCVD technology at ANL





- More stable plasmas
- New plasma Chemistries
- Higher operating pressures (e.g. higher growth rates)

iplas

Task 2B Carbon Nanocomposites

Goal

- Synthesis of carbon nanofiber and hybrid nanofiber/diamond structures with unique mechanical, tribological, and electronic properties.

Team

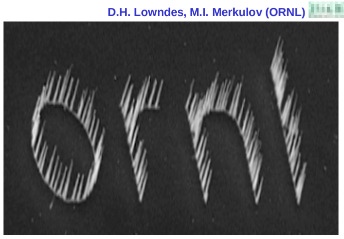
ORNL	Synthesis of vertically aligned carbon nanofiber arrays
ANL	Deposition of UNCD on nanofiber catalysts or pre-synthesized nanofiber arrays; Field Emission Studies
NU	Novel plasma chemistries (UNCD/Nanotubes); TEM Holography
NCSU	PEEM/FEEM studies of field emission properties

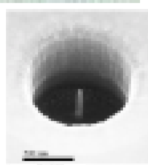
Key issues

- Optimize growth of nanofiber array
- Growth of UNCD/nanofiber/nanotube composites
- Transport properties (electronic, field emission) of composites

Vertically aligned carbon nanofibers (VACNFs)

D.H. Lowndes, M.I. Merkulov (ORNL)





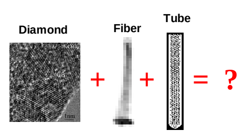
Gated VACNF Cathode Structure

- **A patterned metal catalyst thin film is deposited on the substrate**
- **Plasma enhanced CVD (PECVD) used to grow arrays of individual VACNFs**
- **VACNF growth is "from the tip"**
- **Catalyst dot pattern, size, and growth time determine nanofiber location, diameter, size**

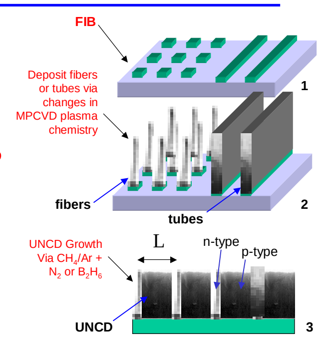
Carbon Nanocomposites

Vision

- What if one could *strategically* combine sp^3 and sp^2-bonded carbon in a material?



- UNCD/Nanofibers/Nanotubes: All synthesized via plasma CVD
  - Change plasma chemistry to control sp^3/sp^2 ratio and/or morphology
- Mechanical, Tribological, **Electrical**, Optical Properties?

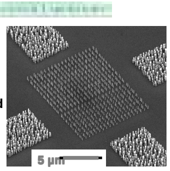


Confinement? Proximity?

Carbon-based Nanocomposites: TEAMING

Grow patterned arrays of carbon nanofibers

Provide patterned templates for UNCD/nanotube growth



SEM imaging of Field emission sites

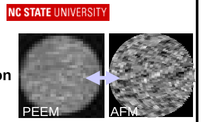
ARGONNE NORTHWESTERN UNIVERSITY

Grow UNCD/fibers/tubes On ORNL-prepared substrates and VACNF arrays

Field Emission Studies

NC STATE UNIVERSITY

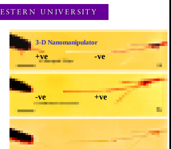
Field emission properties



Compare PEEM, FEEM, AFM

NORTHWESTERN UNIVERSITY

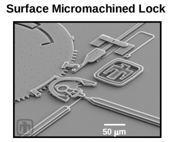
Conduct TEM holography studies to image electron densities in nanocomposites during field emission



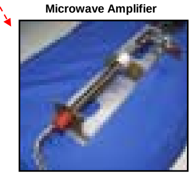
Potential Technological Applications & Industrial Partners

- MEMS
- Cold-Cathode Electron Sources
- Bio-Electrodes
- Chemical Process Pumps
  - Flowserve

Surface Micromachined Lock

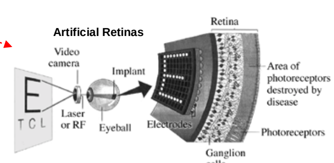


Microwave Amplifier



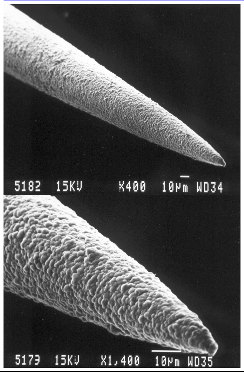
Northrop Grumman

Artificial Retinas



Second Sight

New Result: UNCD coating of W bio-electrode



- $Ar/CH_4/N_2/H_2$ plasma
- Conductive diamond coating
- Add Hydrogen to achieve uniform heating

Management Plan

- Center coordinators
  - Dieter Gruen/John Carlisle - ANL
  - Thomas Friedmann - SNL
- Funding - \$300K / Year
  - Three post docs and four graduate students
  - Post docs/Students to work on collaborative projects
  - \$15K - annual workshop
- Conference calls - Videoconferencing - Website
- Annual workshop to recalibrate priorities/budget

Budget

Institution	Funding (\$1,000's)	Type of Support	Task/Project
ANL	\$65 15	Postdoc Graduate Student (Theory)	Task 2B, 1A, 1B Task 2A
SNL	65	Postdoc	Task 1A, 1B
ORNL	65	Postdoc	Task 2B
LBNL	25	Graduate Student	Task 1B, 1A
NU	25	Graduate Student	Task 2B, 2A
NCSU	25	Graduate Student	Task 2A, 2B
All	15	Annual Workshop (coordinated by ANL/SNL)	All
TOTAL	\$300		

All Funding used to support postdocs, graduate students

- TASK 1A:
  - Postdoc_{SNL}
  - Postdoc_{ANL}
  - $\text{Gradstudent}_{LBNL}$
- TASK 1B:
  - $\text{Gradstudent}_{LBNL}$
  - Postdoc_{SNL}
  - Postdoc_{ANL}
- TASK 2A:
  - Postdoc_{ANL}
  - $\text{Gradstudent}_{NCSU}$
  - Gradstudent_{NU}
- TASK 2B:
  - Postdoc_{ORNL}
  - Gradstudent_{NU}
  - $\text{Gradstudent}_{NCSU}$

Summary

- Scientific excellence
- Involvement of several laboratories
  - Brings together the top DOE programs in this area at DOE laboratories as well as universities
- Clear relationship to energy and DOE technologies
  - EE/transportation technologies - advanced electronics
  - EE/power technologies – power systems
  - Energy efficiency – mechanical pumps, sensors
  - Defense Program – advanced microsystems, sensors
- Partnerships with industry